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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Rinze BENEDICTUS et al.

Serial No.: 10/821,184

Filed: April 9, 2004

TITLE: AN Al-Zn-Mg-Cu ALLOY WITH IMPROVED DAMAGE TOLERANCE-STRENGTH COMBINATION PROPERTIES

CLAIM FOR PRIORITY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

The benefit of the filing date of the following prior foreign application filed in the following foreign country is hereby requested for the above-identified application and the priority provided in 35 USC 119 is hereby claimed:

European Appln. No.03076048.2, Filed April 10, 2003.

In support of this claim, a certified copy of said original foreign application and a Verified English Translation are filed herewith.

It is requested that the file of this application be marked to indicate that the requirements of 35 USC 119 have been fulfilled and that the Patent and Trademark Office kindly acknowledge receipt of this document.

Respectfully submitted,

Date: June 28, 2004

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Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03076048.2

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 03076048.2
Demande no:

Anmeldetag:
Date of filing: 10.04.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

An Al-Zn-Mg-Cu alloy with improved damage tolerance-strength combination properties

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C22C21/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

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AN Al-Zn-Mg-Cu ALLOY WITH IMPROVED DAMAGE TOLERANCE-STRENGTH COMBINATION PROPERTIES.

FIELD OF THE INVENTION

The invention relates to a wrought Al-Zn-Mg-Cu aluminium type (or 7000- or 7xxx- series aluminium alloys as designated by the Aluminum Association). More specifically, the present invention is related to an age-hardenable, high strength, high fracture toughness and highly corrosion resistant aluminium alloy and products made of that alloy. Products made from this alloy are very suitable for aerospace applications, but not limited to that. The alloy can be processed to various product forms (e.g. sheet, thin plate, thick plate, extruded or forged products).

In every product form, made from this alloy, property combinations can be achieved that are outperforming products made from nowadays known alloys. Because of the present invention, the uni-alloy concept can now be used also for aerospace applications. This will lead to significant cost reduction in the aerospace industry. Recycleability of the aluminium scrap produced during the production of the structural part or at the end of the life-cycle of the structural part will become significant easier because of the uni-alloy concept.

BACKGROUND OF THE INVENTION

Different types of aluminium alloys have been used in the past for forming a variety of products for structural applications in the aerospace industry. Designers and manufacturers in the aerospace industry are constantly trying to improve fuel efficiency, product performance and constantly trying to reduce the manufacturing and service costs. The preferred method for achieving the improvements, together with the cost reduction, is the uni-alloy concept, i.e. one aluminium alloy that is capable of having improved property balance in the relevant product forms.

The alloy members and temper designations used herein are in accordance with the well-known aluminium alloy product standards of the Aluminum Association.

State of the art at this moment is high damage tolerant AA2x24 (i.e. AA2524) or AA6x13 or AA7x75 for fuselage sheet, AA2324 or AA7x75 for lower wing, AA7055 or AA7449 for upper wing and AA7050 or AA7010 or AA7040 for wing spars and ribs or other sections machined from thick plate. The main reason for using different alloys for each different application is the difference in the property balance

for optimum performance of the whole structural part.

For fuselage skin, damage tolerant properties under tensile loading are considered to be very important, that is a combination of fatigue crack growth rate ("FCGR"), plane stress fracture toughness and corrosion. Based on these property requirements, high damage tolerant AA2x24-T351 (see e.g. US-5,213,639, EP-1026270-A1) or Cu containing AA6xxx-T6 (see e.g. US-4.,89,932, US-5,888,320, US-2002/0039664-A1, EP-1143027-A1) would be the preferred choice of civilian aircraft manufactures.

For lower wing skin a similar property balance is desired, but some toughness is allowably sacrificed for higher tensile strength. For this reason AA2x24 in the T39 or a T8x temper are considered to be logical choice (see e.g. US-5,865,914, US-5,593,516, EP-1114877-A1), although AA7x75 in the same temper is sometimes also applied.

For upper wing, where compressive loading is more important than the tensile loading, the compressive strength, fatigue (SN-fatigue or life-time) and fracture toughness are the most critical properties. Currently, the preferred choice would be AA7150, AA7055, AA7449 or AA7x75 (see e.g. US-5,221,377, US-5,865,911, US-5,560,789, US-5,312,498). These alloys have high compressive yield strength with at the moment acceptable corrosion resistance and fracture toughness, although aircraft designers would welcome improvements on these property combinations.

For thick sections having a thickness of more than 3 inch or parts machined from such thick sections, a uniform and reliable property balance through thickness is important. Currently, AA7050 or AA7010 or AA7040 (see US-6,027,582) or C80A (see US-2002/0150498-A1) are used for this type of applications. Reduced quench sensitivity (that is deterioration of properties through thickness with lower quenching speed or thicker products) is a major wish from the aircraft manufactures. Especially the properties in the ST-direction are a major concern of the designers and manufactures of structural parts.

A better performance of the aircraft (i.e. reduced manufacturing cost and reduced operation cost) can be achieved by improving the property balance of the aluminium alloys used in the structural part and preferably using only one type of alloy to reduce the cost of the alloy and to reduce the cost in the recycling of aluminium scrap and waste.

Accordingly, it is believed that there is a demand for an aluminium alloy capable of achieving the improved proper property balance in every relevant product form.

SUMMARY OF INVENTION

The present invention is directed to an AA7xxx-series aluminium alloy having the capability of achieving a property balance in any relevant product that is better than property balance of the variety of commercial aluminium alloys (AA2xxx, AA6xxx, AA7xxx) nowadays used for those products.

A preferred composition of the alloy of the present invention consists essentially of, in weight %, about 6.5 to 9.5 zinc (Zn), about 1.2 to 2.2 % magnesium (Mg), about 1.0 to1.9% copper (Cu), about 0 to 0.5% zirconium (Zr), about 0 to 0.7% scandium (Sc), about 0 to 0.4% chromium (Cr), about 0 to 0.3% hafnium (Hf), about 0 to 0.4% titanium (Ti), about 0 to 0.8% manganese (Mn), the balance being aluminium (Al) and other incidental elements. And is a preferred embodiment with the limitation of $0.9Mg-0.6 \leq Cu \leq 0.9Mg+0.05$.

A more preferred alloy composition according to the invention consist essentially of, in weight %, about 6.5 to 7.9% Zn, about 1.4 to 2.10% Mg, about 1.2 to 1.80% Cu, and preferably wherein $0.9Mg-0.5 \leq Cu \leq 0.9Mg$, about 0 to 0.5% Zr, about 0 to 0.7% Sc, about 0 to 0.4% Cr, about 0 to 0.3% Hf, about 0 to 0.4% Ti, about 0 to 0.8% Mn, the balance being Al and other incidental elements.

A more preferred alloy composition according to the invention consist essentially of, in weight %, about 6.5 to 7.9% Zn, about 1.4 to 1.95% Mg, about 1.2 to 1.75% Cu, and preferably wherein $0.9Mg-0.5 \leq Cu \leq 0.9Mg-0.1$, about 0 to 0.5% Zr, about 0 to 0.7% Sc, about 0 to 0.4% Cr, about 0 to 0.3% Hf, about 0 to 0.4% Ti, about 0 to 0.8% Mn, the balance being aluminium and other incidental elements.

In a more preferred embodiment, the lower limit for the Zn-content is 6.7%, and more preferably 6.9%.

The above mentioned aluminium alloys may contain impurities or incidental or intentionally additions, such as for example up to 0.3% Fe, preferably up to 0.14% Fe, up to 0.2% silicon (Si), and preferably up to 0.12% Si, up to 1% silver (Ag), up to 1% germanium (Ge), up to 0.4% vanadium (V). The other additions are generally governed by the 0.05-0.15 weight % ranges as defined in the Aluminium Association, thus each unavoidable impurity in a range <0.05%, and the total of

impurities <0.15%.

The dispersoid forming elements like for example Zr, Sc, Hf, Cr and Mn are added to control the grain structure and the quench sensitivity. The optimum levels of dispersoid formers do depend on the processing, but when one single chemistry of main elements (Zn, Cu and Mg) is chosen within the preferred window and that chemistry will be used for all relevant products form, then Zr levels are preferably less than 0.11%.

A preferred maximum for the Zr level is a maximum of 0.15%. A suitable range of the Zr level is a range of 0.04 to 0.15%. A more preferred upper-limit for the Zr addition is 0.13%, and even more preferably not more than 0.11%.

The addition of Sc is preferably not more than 0.3%, and preferably not more than 0.18%. When combined with Sc, the sum of Sc + Zr should be less then 0.3%, preferably less than 0.2%, and more preferably at a maximum of 0.17%, in particular where the ratio of Zr and Sc is between 0.7 and 1.4.

Another dispersiod former that can be added, alone or with other dispersiod formers is Cr. Cr levels should be preferable below 0.3%, and more preferably at a maximum of 0.20%, and even more preferably 0.15%. When combined with Zr, the sum of Zr + Cr should not be above 0.20%, and preferably not more than 0.17%.

The preferred sum of Sc + Zr + Cr should not be above 0.4%, and more preferably not more than 0.27%.

Also Mn can be added alone or in combination with one of the other dispersoid formers. A preferred maximum for the Mn addition is 0.4%. A suitable range for the Mn addition is in the range of 0.05 to 0.40%, and preferably 0.12 to 0.30%. A preferred lower limit for the Mn addition is 0.12%, and more preferably 0.15%. When combined with Zr, the sum of Mn + Zr should be less then 0.4%, preferably less than 0.32%, and a suitable minimum is 0.14%.

In another embodiment of the aluminium alloy product according to the invention the alloy is free of Mn, in practical terms this would mean that the Mn-content is < 0.02%, and preferably < 0.01%, and more preferably the alloy is essentially free from Mn.

In a particular embodiment of the wrought alloy according to this invention, the alloy consists essentially of, in weight percent:

Zn 7.2 to 7.7, and typically about 7.43

Mg 1.79 to 1.92, and typically about 1.83

Cu 1.43 to 1.52, and typically about 1.48

Zr or Cr 0.06 to 0.10, typically 0.08

Mn optionally in a range of 0.09 to 0.19, or alternatively < 0.02

Si < 0.07, and typically about 0.04

Fe < 0.08, and typically about 0.05

Ti < 0.01, and typically about 0.01

balance aluminium.

In another particular embodiment of the wrought alloy according to this invention, the alloy consists essentially of, in weight percent:

Zn 7.2 to 7.7, and typically about 7.43

Mg 1.90 to 1.97, and typically about 1.94

Cu 1.43 to 1.52, and typically about 1.48

Zr or Cr 0.06 to 0.10, and typically 0.08

Mn optionally in a range of 0.09 to 0.19, or alternatively < 0.02

Si < 0.07, and typically about 0.05

Fe < 0.08, and typically about 0.06

Ti < 0.01, and typically about 0.01

balance aluminium.

The alloy according to the invention can be prepared by conventionally melting and may be (direct chill, D.C.) cast into ingot form. Grain refiners such as titanium boride or titanium carbide may also be used. After scalping and possible homogenisation, the ingots are further processed by, for example extrusion or forging or hot rolling in one or more stages. This processing may be interrupted for an inter-anneal. Further processing may be cold working, which may be cold rolling or stretching. The product is solution heat treated and quenched by immersion in or spraying with cold water or fast cooling to a temperature lower than 95°C. The product can be further processed, for example rolling or stretching, for example up to 8%, or may be stress relieved by stretching or compression and/or aged to a final or intermediate temper. The product may be shaped or machined to the final or intermediate structure, before or after the final ageing or even before solution heat treatment.

DETAILED DESCRIPTION OF THE INVENTION

The design of commercial aircraft requires different sets of properties for different types of structural parts. An alloy when processed to various product forms (i.e., sheet, plate, thick plate, forging or extruded profile etc.) and to be used in a wide variety of structural parts with different loading sequences in service life and consequently meeting different material requirements for all those product forms, must be unprecedented versatile.

The important material properties for a fuselage sheet product are the damage tolerant properties under tensile loads (i.e. FCGR, fracture toughness and corrosion resistance).

The important material properties for a lower wing skin in a high capacity and commercial jet aircraft are similar to those for a fuselage sheet product, but typically a higher tensile strength is wished by the aircraft manufactures. Also fatigue life becomes a major material property.

Because the airplane flies at high altitude where it is cold, fracture toughness at minus 65°F is a concern in new designs of commercial aircrafts. Additional desirable features include age formability whereby the material can be shaped during artificial aging, together with good corrosion performance in the areas of stress corrosion cracking resistance and exfoliation corrosion resistance.

The important material properties for an upper wing skin product are the properties under compressive loads, i.e. compressive yield strength, fatigue life and corrosion resistance.

The important material properties for machined parts from thick plate depend on the machined part. But, in general, the gradient in material properties through thickness must be very small and the material properties like strength, fracture toughness, fatigue and corrosion resistance must be a high level.

The present invention is directed at an alloy composition when processed to a variety of products, such as, but not limited to, sheet, plate, thick plate etc, will meet or exceed the desired material properties. The property balance of the product will out-perform the property balance of the product made from nowadays commercially used alloys.

It has been found very surprisingly a chemistry window within the AA7000 window, unexplored before, that does fulfil this unique capability.

The present invention resulted from an investigation on the effect of Cu, Mg and Zn levels, combined with various levels and types of dispersoid former (e.g. Zr, Cr, Sc, Mn) on the phases formed during processing. Some of these alloys were processed to sheet and plate and tested on tensile, Kahn-tear toughness and corrosion resistance. Interpretations of these results lead to the surprising insight that an aluminium alloy with a chemical composition within a certain window, will exhibit excellent properties as well as for sheet as for plate as for thick plate as for extrusions as for forgings.

In another aspect of the invention there is provided a method of manufacturing the aluminium alloy product according to the invention. The method of manufacturing a high-strength, high-toughness AA7000-series alloy product having a good corrosion resistance, comprising the processing steps of:

a.) casting an ingot having a composition as set out in the description and claims;

b.) homogenising and/or pre-heating the ingot after casting;

c.) hot working the ingot into a pre-worked product;

d.) optional reheating the pre-worked product and either,

e.) hot working and/or cold working to a desired workpiece form;

f.) solution heat treating said formed workpiece at a temperature and time sufficient to place into solid solution essentially all soluble constituents in the alloy;

g.) quenching the solution heat treated workpiece by one of spray quenching or immersion quenching in water or other quenching media;

h.) optionally stretching or compressing of the quenched work piece or otherwise cold worked to relieve stresses, for example levelling of sheet products;

i.) artificially ageing the quenched and optionally stretched or compressed workpiece to achieve a desired temper, for example, the tempers T6, T74, T76, T751, T7451, T7651, T77 and T79.

The alloy products of the present invention are conventionally prepared by melting and may be direct chill (D.C.) cast into ingots or other suitable casting techniques. Homogenisation treatment is typically carried out in one or multi steps, each step having a temperature in the range of 460 to 490°C. The pre-heat temperature involves heating the rolling ingot to the hot-mill entry temperature, which is typically in a temperature range of 400 to 460°C. Hot working the alloy product can be done by one of rolling, extruding or forging. For the current alloy hot rolling is being

preferred. Solution heat treatment is typically carried out in the same temperature range as used for homogenisation, although the soaking times can be chosen somewhat shorter.

A surprisingly excellent property balance is being obtained in whatever thickness is produced. In the sheet thickness range of up to 1.5 inch the properties will be excellent for fuselage sheet, and preferably the thickness is up to 1 inch. In the thin plate thickness range of 0.7 to 3 inch the properties will be excellent for wing plate, e.g. lower wing plate. The thin plate thickness range can be used also for stringers or to form an integral wing panel and stringer for use in an aircraft wing structure. More peak-aged material will give an excellent upper wing plate, whereas slightly more over-ageing will give excellent properties for lower wing plate. When processed to thicker gauges of more than 2.5 inch up to about 11 inch excellent properties will be obtained for integral part machined from plates, or to form an integral spar for use in an aircraft wing structure, or in the form of a rib for use in an aircraft wing structure. The thicker gauge products can be used also as tooling plate, e.g. moulds for manufacturing formed plastic products, for example via die-casting or injection moulding. The alloy products according to the invention can also be provided in the form of a stepped extrusion or extruded spar for use in an aircraft structure, or in the form of a forged spar for use in an aircraft wing structure. Surprisingly, all these products with excellent properties can be obtained from one alloy with one single chemistry.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an Mg-Cu diagram setting out the Cu-Mg range for the alloy according to this invention, together with narrower preferred ranges;

Fig. 2 is a diagram comparing the fracture toughness vs. the tensile yield strength for the alloy product according to the invention against several references;

Fig. 3 is a diagram comparing the fracture toughness vs. the tensile yield strength for the alloy product according to this invention in a 30 mm gauge against two references;

Fig. 4 is a diagram comparing the plane strain fracture toughness vs. the tensile yield strength for the alloy products according to the invention using different processing routes.

Fig. 1 shows schematically the ranges for the Cu and Mg for the alloy

according to the present invention in their preferred embodiments as set out in dependent claims 2 to 4. Also shown are two narrower more preferred ranges. The ranges can also be identified by using the corner-points A, B, C, D, E, and F of a hexagon box. Preferred range are identified by A' to F', and more preferred ranges by A" to F". The coordinates are listed in Table 1. In Fig. 1 also the alloy composition according to this invention as mentioned in the examples hereinafter are illustrated as individual points.

Table 1. Coordinates (in wt.%) for the corner-points of the Cu-Mg ranges for the preferred ranges of the alloy product according to the invention.

Corner point	(Mg, Cu) wide range	Corner point	(Mg, Cu) preferred range	Corner point	(Mg, Cu) more preferred range
A	1.20, 1.00	A'	1.40, 1.10	A"	1.40, 1.10
B	1.20, 1.13	B'	1.40, 1.26	B"	1.40, 1.16
C	2.05, 1.90	C'	2.05, 1.80	C"	2.05, 1.75
D	2.20, 1.90	D'	2.10, 1.80	D"	2.10, 1.75
E	2.20, 1.40	E'	2.10, 1.40	E"	2.10, 1.40
F	1.77, 1.00	F'	1.78, 1.10	F"	1.87, 1.10

EXAMPLES

Example 1.

On a laboratory scale alloys were cast to proof the principle of the current invention and processed to 4.0 mm sheet or 30 mm plate. The alloy compositions are listed in Table 2, for all ingots Fe < 0.06, Si < 0.04, Ti 0.01, balance aluminium. Rolling blocks of approximately 80 by 80 by 100mm (height x width x length) were sawn from round lab cast ingots of about 12kg. The ingots were homogenised at 460±5°C for about 12 hrs and consequently at 475±5°C for about 24 hrs and consequently slowly air cooled to mimic an industrial homogenisation process. The rolling ingots were pre-heated for about 6 hrs at 410±5°C. At an intermediate thickness range of about 40 to 50 mm the blocks were re-heated at 410±5°C. Some blocks were hot rolled to the final gauge of 30 mm, others were hot rolled to a final

gauge of 4.0mm. During the whole hot-rolling process, care was taken to mimic an industrial scale hot rolling. The hot-rolled products were solution heat treated and quenched. Most were quenched in water, but some were also quenched in oil to mimic the mid and quarter-thickness quenching-rate of a 6-inch thick plate. The products were cold stretched by about 1.5% to relieve the residual stresses. The ageing behaviour of the alloys was investigated. The final products were over-aged to a near peak aged strength (e.g. T76 or T77 temper).

Tensile properties have been tested according EN10.002. The tensile specimens from the 4 mm thick sheet were flat EURO-NORM specimen with 4 mm thickness. The tensile specimens from the 30 mm plate were round tensile specimens taken from mid-thickness. The tensile test results in Table 1 are from the L-direction. The Kahn-tear toughness is tested according ASTM B871-96. The test direction of the results on Table 2 is the T-L direction. The so-called notch-toughness can be obtained by dividing the tear-strength, obtained by the Kahn-tear test, by the tensile yield strength ("TS/Rp"). This typical result from the Kahn-tear test is known in the art to be a good indicator for true fracture toughness. The unit propagation energy ("UPE"), also obtained by the Kahn-tear test, is the energy needed for crack growth. It is believed that the higher the UPE, the more difficult to grow the crack, which is a desired feature of the material.

To qualify for a good corrosion performance, the exfoliation corrosion resistance ("EXCO") when measured according ASTM G34-97 must be at least "EA" or better. The inter-granular corrosion ("IGC") when measured according MIL-H-6088 is preferable absent. Some pitting is acceptable, but preferably should be absent also.

In order to have a promising candidate alloy suitable for a variety of products, it had to fulfil the following requirements on lab-scale: A tensile yield strength of at least 510 MPa, an ultimate strength of at least 560 MPa, a notch toughness of at least 1.5 and a UPE of at least 200 kJ/m^2. The results for the various alloys as function some processing are listed in Table 2.

In order to meet all those desired material properties, the chemistry of the alloy has to be carefully balanced. According to the present results, too high values for Cu, Mg and Zn contents were found to be detrimental to toughness and corrosion resistance. Whereas too low values were found to be detrimental for high strength

levels.

But, very surprisingly, a higher Zn-level is increasing the toughness and crack growth resistance. Therefore, it is desirable to use higher Zn level and combine these with lower Mg and Cu levels. It has been found that the Zn-content should not be below 6.5%, and preferably not below 6.7%, and more preferably not below 6.5%.
Mg is required to have acceptable strength levels. It has been found that a ratio of Mg/Zn of about 0.25 or lower seems to give the best strength-toughness combination. However, Mg levels should not exceed 2.2%, and preferably not exceed 2.1%, and even more preferably not exceed 1.95%. This upper-limit is lower than in the conventional AA-windows or ranges of presently used commercial aerospace alloys like AA7050, AA7010 and AA7075.
In order to have a desirably very high crack growth resistance (or UPE) Mg levels must be carefully balanced and should be preferable be in the same order or slightly more than the Cu levels, and preferably $(0.9xMg - 0.6) \leq Cu \leq (0.9xMg + 0.05)$. The Cu-content should not be too high. It has been found that the Cu-content should not be higher than 1.9%, and preferably should not exceed 1.80%, and more preferably not exceed 1.75%.

The dispersiod formers used in AA7xxx-series alloys are typically Cr, as in e.g. AA7x75, or Zr, as in e.g. AA7x50 and AA7x10. Conventionally, Mn is believed to be detrimental for toughness, but much to our surprise, a combination of Mn and Zr shows still a very good strength-toughness balance.

Example 2.

A batch of full-size rolling ingots with a thickness of 440mm thick on an industrial scale were produced by a DC-casting and having the chemical composition (in wt.%): 7.43% Zn, 1.83% Mg, 1.48% Cu, 0.08% Zr, 0.02% Si and 0.04% Fe, balance aluminium and unavoidable impurities. One of these ingots was scalped, homogenised at 12hrs/470°C + 24hrs/475°C + air cooled to ambient temperature. This ingot was pre-heated at 8hrs/410°C and then hot rolled to about 65mm. The rolling block was then turned 90 degrees and further hot rolled to about 10mm. Finally the rolling block was cold rolled to a gauge of 5.0mm. The obtained sheet was solution heat treated at 475°C for about 40 minutes, followed by water-spray quenching. The resultant sheets were stress relieved by a cold stretching operation of

about 1.8%. Two ageing variants have been produced, variant A: for 5hrs/120°C + 9hrs/155°C, and variant B: for 5hrs/155°C + 9hrs/165°C.

The tensile results have been measured according EN 10.002. The compression yield strength ("CYS") has been measured according ASTM E9-89a. The shear strength has been measured according ASTM B831-93. The fracture toughness, Kapp, has been measured according ASTM E561-98 on 16-inch wide centre cracked panels [M(T) or CC(T)]. The Kapp has been measured at ambient room temperature (RT) and at –65°F. As reference material a high damage tolerant ("HDT") AA2x24-T351 has been tested as well. The results are listed in Table 3.

The exfoliation corrosion resistance has been measured according ASTM G34-97. Both variant A as B showed EA rating.

The inter-granular corrosion measured according MIL-H-6088 for variant A was about 70 μm and for variant B about 45 μm. Both are significantly lower than the typical 200 μm as measured for the reference AA2x24-T351.

From Table 3 it can be seen that there is a significant improvement with the alloy according to the invention. A significant increase in strength at comparable or even higher fracture toughness levels. Also at a low temperature of minus 65°F, outperforms the nowadays standard high damage tolerant fuselage alloy AA2x24-T351. Note that also the corrosion resistance of the inventive alloy is significant better than the AA2x24-T351.

The fatigue crack growth rate ("FCGR") has been measured according ASTM E647-99 on 4-inch wide compact tension panels [C(T)] with an R-ratio of 0.1. In Table 3 the da/dn per cycle at a stress range of $\Delta K = 27.5$ ksi.in$^{0.5}$ (= about 30 MPa.m$^{0.5}$) of the inventive alloy has been compared with the reference high damage tolerant AA2x24-T351.

It can be clearly seen from the results in Table 4 that the crack growth of the inventive alloy is better than that of the high damage tolerant AA2x24-T351.

Example 3.

Another full-scale ingot taken from the batch DC-cast from Example 2 was produced into a plate of 6-inch thickness. Also this ingot was scalped, homogenised at 12hrs/470°C + 24hrs/475°C + air cooled to ambient temperature. The ingot was pre-heated at 8hrs/410°C and then hot rolled to about 152mm. The obtained hot-

rolled plate was solution heat treated at 475°C for about 7 hours followed by water-spray quenching. The plates were stress relieved by a cold stretching operation of about 2.0 %. Several different two-step ageing processes have been applied.

The tensile results' have been measured according EN 10.002. The specimens were taken from the T/4-position. The plane strain fracture toughness, Kq, has been measured according ASTM E399-90. If the validity requirements as given in ASTM E399-90 are met, these Kq values are a real material property and called K_{1C}. The K_{1C} has been measured at ambient room temperature ("RT"). The exfoliation corrosion resistance has been measured according ASTM G34-97. The results are listed in Table 5. All ageing variants as shown in Table 5 showed "EA" rating.

In Fig. 2 a comparison is given versus results presented in prior art document US-2002/0150498-A1, Table 2, incorporated herein by reference. In this US patent application an example (example 1) if given of a similar product, but with a different chemistry that is stated to be optimised for quench sensitivity. In our inventive alloy we have obtained a similar tensile versus toughness balance as in this US patent application. However, our inventive alloys shows at least superior EXCO resistance. Furthermore, also the elongation of our inventive alloy is superior to that disclosed in US2-002/0150498-A1, Table 2. The overall property balance of alloy according to the present invention when processed to 6-inch thick plate is better that that disclosed in US-2002/0150498-A1. In Fig. 2 also documented data for thick gauges of 75 to 220 mm are shown for the AA7050/7010 alloy (see AIMS 03-02-022, December 2001), the AA7050/7040 alloy (see AIMS 03-02-019, September 2001), and the AA7085 alloy (see AIMS 03-02-025, September 2002).

Example 4.

Another full-scale ingot taken from the batch DC-cast from Example 2 was produced to plates of respectively 63.5 mm and 30 mm thickness. The cast ingot was scalped, homogenised at 12hrs/470°C + 24hrs/475°C + air cooled to ambient temperature. The ingot was pre-heated at 8hrs/410°C and then hot rolled to respectively 63.5 and 30 mm. The obtained hot-rolled plates were solution heat treated at 475°C for about 2 to 4 hrs followed by water-spray quenching. The plates were stress relieved by a cold stretching operation of respectively 1.7% and 2.1 % for the 63.5 mm and 30 mm plates. Several different two-step ageing processes have

been applied.

The tensile results have been measured according EN 10.002. The plane strain fracture toughness, Kq, has been measured according ASTM E399-90 on CT-specimens. If the validity requirements as given in ASTM E399-90 are met, these Kq values are a real material property and called K_{IC}. The K_{IC} has been measured at ambient room temperature ("RT"). The exfoliation corrosion resistance has been measured according ASTM G34-97. The results are listed in Table 6. All ageing variants as shown in Table 6 showed "EA"-rating.

In Table 7 the values are given of nowadays state of the art commercial upper wing alloys, and are typical data according to the supplier of that material (Alloy 7150-T7751 plate & 7150-T77511 extrusions, Alcoa Mill products, Inc., ACRP-069-B).

In Fig. 3 a comparison is given of the inventive alloy versus AA7150-T77 and AA7055-T77. From Fig. 3 it can be clearly seen that the tensile versus toughness balance of the current inventive alloy is superior to commercial available AA7150-T77 and also to AA7055-T77.

Example 5.

Another full-scale ingot taken from the batch DC-cast from Example 2 (hereinafter "Alloy A") was produced to plates of 20mm thickness. Also one other casting was made (designated "Alloy B") with a chemical composition (in wt.%): 7.39% Zn, 1.66% Mg, 1.59% Cu, 0.08% Zr, 0.03% Si and 0.04% Fe, balance aluminium and unavoidable impurities. These ingots were scalped, homogenised at 12hrs/470°C + 24hrs/475°C + air cooled to ambient temperature. For further processing, three different routes were used.

Route 1: The ingot of alloy A and B was pre-heated at 6hrs/420°C and then hot rolled to about 20 mm.

Route 2: Ingot of alloy A were pre-heated at 6hrs/460°C and then hot rolled to about 20 mm

Route 3: Ingot of alloy B were pre-heated at 6hrs/420°C and then hot rolled to about 24 mm, subsequently these plates were cold rolled to 20mm.

Thus, four variants were produced and identified as: A1, A2, B1 and B3.

The resultant plates were solution heat treated at 475°C for about 2 to 4 hrs

followed by water-spray quenching. The plates were stress relieved by a cold stretching operation of about 2.1 %. Several different two-step ageing processes have been applied.

The tensile results have been measured according EN 10.002. The plane strain fracture toughness, Kq, has been measured according ASTM E399-90 on CT specimens. If the validity requirements as given in ASTM E399-90 are met, these Kq values are a real material property and called K_{IC}. Note that most of the fracture toughness measurement in this example failed the meet the validity criteria on specimen thickness. The reported Kq values are a conservative with respect to K_{IC}, in other words, the reported Kq values are in fact generally lower than the standard K_{IC} values obtained when specimen size related validity criteria of ASTM E399-90 are satisfied. The exfoliation corrosion resistance has been measured according ASTM G34-97. The results are listed in Table 8. All ageing variants as shown in Table 8 showed "EA"-rating.

The results of Table 8 have are shown graphically in Fig. 4. In Fig 4 lines have been fitted through the data to get an impression of the differences between A1, A2, B1 and B3. From that graph it can be clearly seen that alloy A and B, when comparing A1 and B1, have a similar strength versus toughness behaviour. The best strength versus toughness could be obtained by either B3 (i.e. cold rolling to final thickness) or by A2 (i.e. pre-heat at a higher temperature). Also note that the results of Table 8 show a significant better strength versus toughness balance than AA7150-T77 and AA7055-T77 as listed in Table 7.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made without departing from the spirit or scope of the invention as hereon described.

Table 2.

Specimen No	Invention Alloy (Y/N)	Thickness (mm)	Temper	Mg (wt%)	Cu (wt%)	Zn (wt%)	Zr (wt%)	Others (wt%)	Rp (MPa)	Rm (MPa)	UPE (kJ/m2)	Ts/Rp -
1	yes	30	T77	1,84	1,47	7,4	0,10		587	627	312	1,53
2	yes	30	T76	1,66	1,27	8,1	0,09		530	556	259	1,76
3	yes	4	T76	2,00	1,54	6,8	0,11		517	563	297	1,62
4	no	4	T76	2,00	1,52	5,6	0,01	0,16Cr	473	528	232	1,45
5	no	4	T76	2,00	1,53	5,6	0,06	0,08Cr	464	529	212	1,59
6	yes	4	T76	1,82	1,68	7,4	0,10		594	617	224	1,44
7	yes	30	T76	2,09	1,30	8,2	0,09		562	590	304	1,64
8	yes	4	T77	2,20	1,70	8,7	0,11		614	626	115	1,38
9	yes	4	T77	1,81	1,69	8,7	0,10		574	594	200	1,47
10	no	4	T76	2,10	1,54	5,6	0,07		490	535	245	1,53
11	no	4	T76	2,20	1,90	6,7	0,10		563	608	-	1,07
12	no	4	T76	1,98	1,90	6,8	0,09		559	592	-	1,32
13	no	4	T77	2,10	2,10	8,6	0,10		623	639	159	1,31
14	no	4	T77	2,50	1,70	8,7	0,10		627	643	117	1,33
15	no	4	T77	1,70	2,10	8,6	0,12		584	605	139	1,44
16	no	4	T77	1,70	2,40	8,6	0,11		598	619	151	1,42
17	no	4	T76	2,40	1,54	5,6	0,01		476	530	64	1,42
18	no	4	T76	2,30	1,54	5,6	0,07		488	542	52	1,54
19	no	4	T76	2,30	1,52	5,5	0,14		496	543	155	1,66
20	yes	4	T76	2,19	1,54	6,7	0,11	0,16Mn	521	571	241	1,65
21	no	4	T76	2,12	1,51	5,6	0,12		471	516	178	1,42

Table 3.

	Ageing	L-TYS (MPa)	LT-TYS (MPa)	L-UTS (MPa)	LT-UTS (MPa)	L-T CYS (MPa)	T-L CYS (MPa)
INV	variant A	544	534	562	559	554	553
INV	variant B	489	472	526	512	492	500
HDT-2x24	T351	360	332	471	452	329	339

	Ageing	L-T Shear (MPa)	T-L Shear (MPa)	RT L-T Kapp (MPa $m^{0.5}$)	RT T-L Kapp (MPa $m^{0.5}$)	-65 F L-T Kapp (MPa $m^{0.5}$)	-65 F T-L Kapp (MPa $m^{0.5}$)
INV	variant A	372	373	103	100	-	-
INV	variant B	340	338	132	127	102	103
HDT-2x24	T351	328	312	-	101	-	103

Table 4. Crack growth per cycle at a stress range of $\Delta K = 27.5$ ksi $in^{0.5}$

INV	variant A	L-T	96%
INV	"	T-L	84%
INV	variant B	L-T	73%
INV	"	T-L	74%
HDT-2x24	T351	L-T	100%

Table 5.

Ageing Proces	L-TYS (MPa)	L-UTS (MPa)	Elong (%)	L-T K1C (MPa m0.5)	EXCO
5hrs/120°C + 11hrs/165°C	453	497	9,9	-	EA
5hrs/120°C + 13hrs/165°C	444	492	12,5	44,4	EA
5hrs/120°C + 15hrs/165°C	434	485	13,0	45,0	EA
5hrs/120°C + 12hrs/160°C	494	523	10,5	39,1	EA
5hrs/120°C + 14hrs/160°C	479	213	8,3	-	EA

Table 6

Thickness (mm)	Ageing	L-TYS (MPa)	L-UTS (MPa)	Elong (%)	L-T K1C (MPa $m^{0.5}$)	LT-TYS (MPa)	LT-UTS (MPa)	Elong (%)	T-L K1C (MPa $m^{0.5}$)
63,5	120-5/150-12	566	594	10,7	42,4	532	572	9,8	32,8
63,5	120-5/155-12	566	599	11,9	40,7	521	561	11,2	33,0
63,5	120-5/160-12	528	569	13,0	51,6	497	516	11,6	40,2
30	120-5/150-12	565	590	14,2	46,9	558	582	13,9	36,3
30	120-5/155-12	557	589	14,4	51,0	547	572	13,6	39,2
30	120-5/160-12	501	548	15,1	65,0	493	539	14,3	46,8

Table 7.: Typical values from ALCOA tech sheet on AA7150-T77 and AA7055-T77, both plates of 25mm

Thickness (mm)	Ageing	L-TYS (MPa)	L-UTS (MPa)	Elong (%)	L-T K1C (MPa $m^{0.5}$)	LT-TYS (MPa)	LT-UTS (MPa)	Elong (%)	T-L K1C (MPa $m^{0.5}$)
25	7150-T77	572	607	12,0	29,7	565	607	11,0	26,4
25	7055-T77	614	634	11,0	28,6	614	641	10,0	26,4

Table 7.

Alloy	Ageing	L-TYS (MPa)	L-UTS (MPa)	L-Elong. (%)	LT-TYS (MPa)	LT-UTS (MPa)	LT-Elong. (%)	T-L K1C (MPa m$^{0.5}$)
B3	120-5/150-10	563	586	13,7	548	581	12,5	38,4
B3	120-5/155-12	558	581	14,4	538	575	13,1	38,7
B3	120-5/160-12	529	563	14,6	517	537	13,7	40,3
B1	120-5/150-10	571	595	13,4	549	581	13,4	36,5
B1	120-5/155-12	552	582	14,3	528	568	13,9	37,1
B1	120-5/160-12	510	552	15,1	493	542	14,5	39,4
A1	120-5/150-10	574	597	13,7	555	590	14,0	33,7
A1	120-5/155-12	562	594	14,4	548	586	13,9	37,1
A1	120-5/160-12	511	556	15,0	502	550	14,3	37,6
A2	120-5/150-10	574	600	14,0	555	595	13,9	36,7
A2	120-5/155-12	552	584	14,3	541	582	13,1	38,0
A2	120-5/160-12	532	572	14,8	527	545	12,4	39,8

CLAIMS

1. An aluminium alloy product with high strength and fracture toughness and a good corrosion resistance, said alloy comprising essentially, in weight %:

Zn	about 6.5 to 9.5
Mg	about 1.2 to 2.2
Cu	about 1.0 to 1.9

optionally one or more of:

Zr	< 0.5
Sc	< 0.7
Cr	< 0.4
Hf	< 0.3
Mn	< 0.8
Ti	< 0.4
V	< 0.4

and the balance being aluminium (Al) and other impurities or incidental elements.

2. Aluminium alloy product according to claim 1, wherein $[(0.9xMg)-0.6] \leq Cu \leq [(0.9xMg) + 0.05]$.

3. Aluminium alloy product according to claim 1, wherein $[(0.9xMg)-0.5] \leq Cu \leq [0.9xMg]$.

4. Aluminium alloy product according to claim 1, wherein $[(0.9xMg)-0.5] \leq Cu \leq [(0.9xMg) - 0.1]$.

5. Aluminium alloy product according any one of claims 1 to 4, wherein

Zn	about 6.5 to 7.9
Mg	about 1.4 to 2.10
Cu	about 1.2 to 1.80

6. Aluminium alloy product according to claim 5, wherein

Zn	about 6.5 to 7.9

Mg	about 1.4 to 1.95
Cu	about 1.2 to 1.75

7. An aluminium alloy product according to any one of the preceding claims, wherein the lower-limit for the Zn-content is 6.7%, and preferably 6.9%.

8. Aluminium alloy product according to any one of the preceding claims, wherein the Zr-content is in a range of up to 0.3%, preferably in a range of up to 0.15%.

9. Aluminium alloy product according to claim 8, wherein the Zr-content is in a range of 0.04 to 0.15%.

10. Aluminium alloy product according to any one of the preceding claims, wherein the Cr-content is in a range of up to 0.3%, preferably in a range of up to 0.15%.

11. Aluminium alloy product according to claim 10, wherein the Cr-content is in a range of 0.04 to 0.15%.

12. Aluminium alloy product according to any one of the preceding claims, wherein the Mn-content is in a range of up to 0.02%.

13. Aluminium alloy product according to any one of the preceding claims 1 to 10, wherein the Mn-content is in a range of 0.05 to 0.30%.

14. Aluminium alloy product according to any one of the preceding claims, wherein the product has an exfoliation corrosion resistance of EA or better.

15. Aluminium alloy product according to any one of the preceding claims, wherein the product is in the form of a sheet, plate, forging or extrusion.

16. Aluminium alloy product according to any one of the preceding claims,

wherein the product is in the form of a sheet, plate, forging or extrusion for use in an aircraft structure.

17. Aluminium alloy product according to any one of the preceding claims, wherein the product is fuselage sheet, upper wing plate, lower wing plate, thick plate for machined parts, forging or thin sheet for stringers.

18. Aluminium alloy product according to any one of the preceding claims, wherein the product has a thickness of greater than 1.5 inches.

19. Aluminium alloy product according to any one of the preceding claims, wherein the product has a thickness of less than 1.5 inches, and preferably has a thickness of less than 1.0 inch.

20. An aluminium alloy product according to any one of claims 1 to 19 processed into a fuselage sheet, wing skin plate and/or thick plate and having essentially the same chemical composition.

21. An aluminium alloy structural component for a commercial jet aircraft, said structural component made from an aluminium alloy product according to any one of claims 1 to 20.

22. Method of producing a high-strength, high-toughness AA7xxx-series alloy product having a good corrosion resistance, comprising the processing steps of:

a.) casting an ingot having a composition according to any one of claims 1 to 14;

b.) homogenising and/or pre-heating the ingot after casting;

c.) hot working the ingot into a pre-worked product;

d.) optional reheating the pre-worked product and either,

e.) hot working and/or cold working to a desired workpiece form;

f.) solution heat treating said formed workpiece at a temperature and time sufficient to place into solid solution essentially all soluble constituents in the alloy;

g.) quenching the solution heat treated workpiece by one of spray quenching or immersion quenching in water or other quenching media;

h.) optionally stretching or compressing of the quenched workpiece;

i.) artificially ageing the quenched and optionally stretched or compressed workpiece to achieve a desired temper.

23. Method of manufacturing according to claim 22, wherein the alloy product has been processed to fuselage sheet.

24. Method of manufacturing according to claim 22, wherein the alloy product has been processed to fuselage sheet having a thickness of less than 1.5 inch.

25. Method of manufacturing according to claim 24, wherein the alloy product has been processed to lower wing plate.

26. Method of manufacturing according to claim 22, wherein the alloy product has been processed to upper wing plate.

27. Method of manufacturing according to claim 22, wherein the alloy product has been processed to an extruded product.

28. Method of manufacturing according to claim 22, wherein the alloy product has been processed to a forged product.

29. Method of manufacturing according to claim 22, wherein the alloy product has been processed to a thick plate having a thickness up to 11 inch.

ABSTRACT

An Al-Zn-Mg-Cu alloy with improved damage tolerance-strength combination properties.

The present invention relates to an aluminium alloy product consists essentially of, in weight %, about 6.5 to 9.5 zinc (Zn), about 1.2 to 2.2 % magnesium (Mg), about 1.0 to1.9 % copper (Cu), preferable $0.9Mg-0.6 \leq Cu \leq 0.9Mg+0.05$, about 0 to 0.5% zirconium (Zr), about 0 to 0.7% scandium (Sc), about 0 to 0.4% chromium (Cr), about 0 to 0.3% hafnium (Hf), about 0 to 0.4% titanium (Ti), about 0 to 0.8% manganese (Mn), the balance being aluminium (Al) and other incidental elements. The invention relates also to a method of manufacturing such as alloy.

1/2

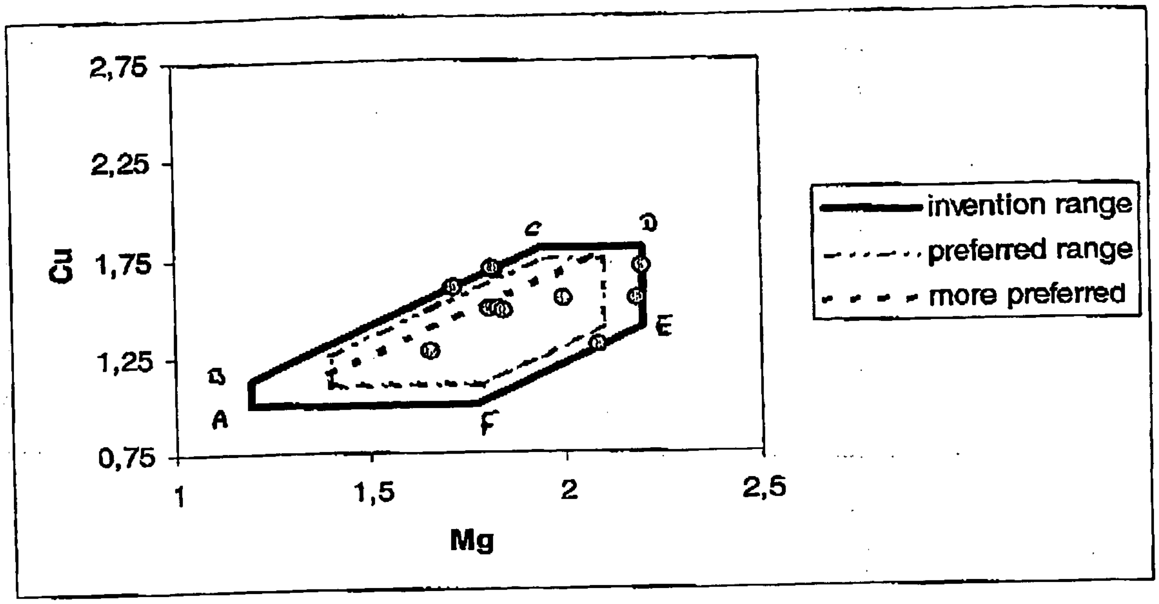
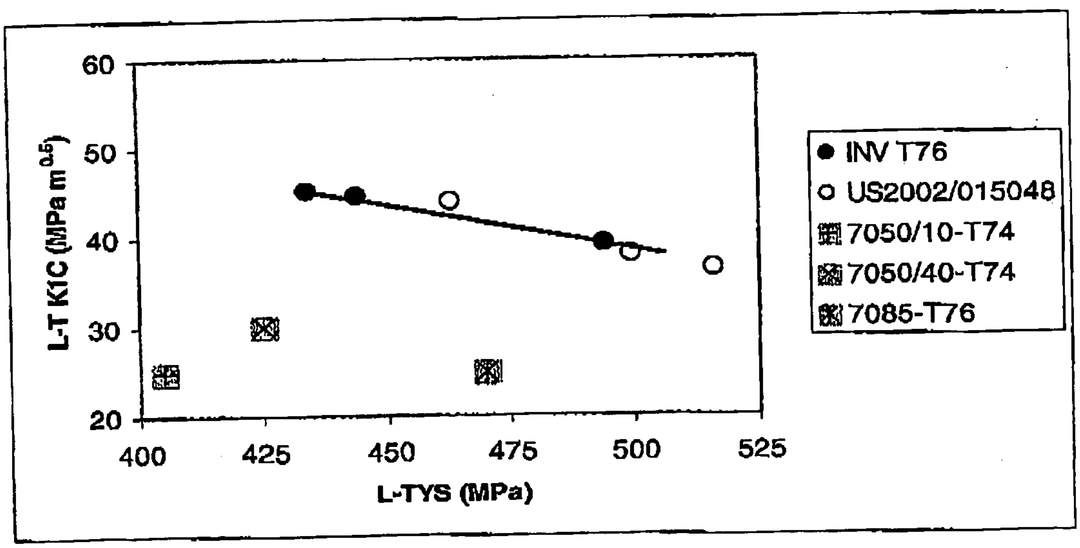

2,75
2,25
1,75
1,25
0,75
Cu
1
1,5
2
2,5
Mg
A
B
C
D
E
F
invention range
preferred range
more preferred

Fig. 1


60
50
40
30
20
L-T K1C (MPa m^0.5)
400
425
450
475
500
525
L-TYS (MPa)
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US2002/015048
7050/10-T74
7050/40-T74
7085-T76

Fig. 2

2/2

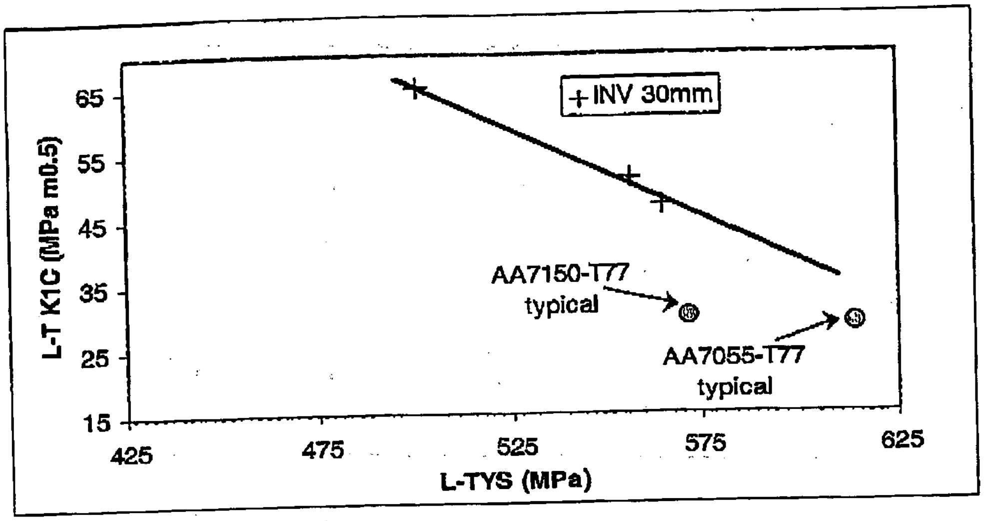
+ INV 30mm
AA7150-T77
typical
AA7055-T77
typical
L-T K1C (MPa m0.5)
L-TYS (MPa)
65
55
45
35
25
15
425
475
525
575
625

Fig. 3

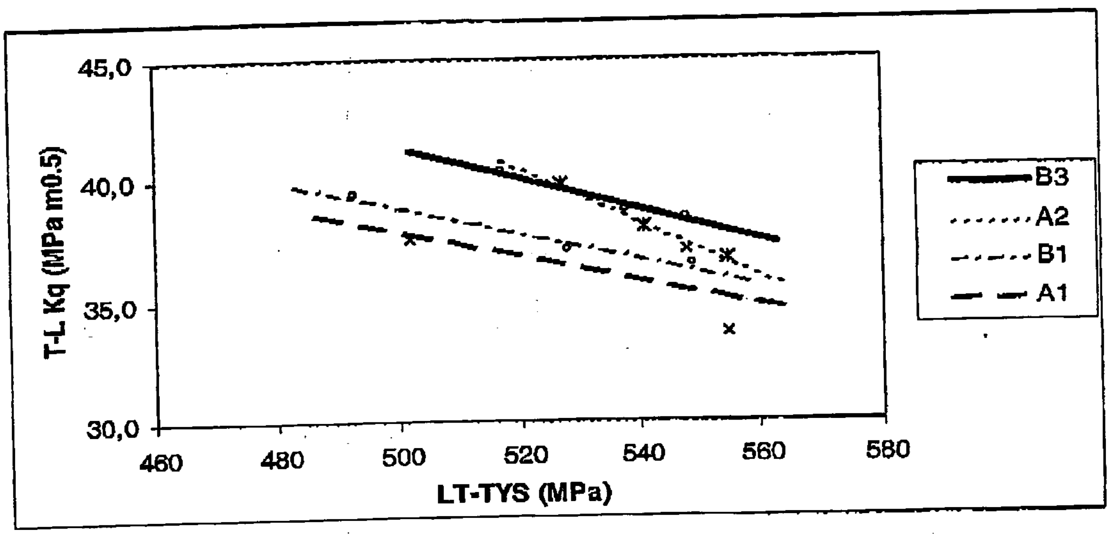
B3
A2
B1
A1
T-L Kq (MPa m0.5)
LT-TYS (MPa)
45,0
40,0
35,0
30,0
460
480
500
520
540
560
580

Fig. 4